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SUBJECT Continued Soviet Research on Organic Insectofungicides /New Work by V K Kuskov and T Kh Gradis

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25X1X 1. [redacted] additional Soviet developments in the field of organic insectofungicides which may be of interest. Mel'nikov and an associate have published another article which is an additional supplement to research and work which he has been doing in this field. The article is titled, "Organic Insectofungicides, XVI, Synthesis of Mixed Esters of Thiophosphoric Acid Containing Various Functional Groups in the Aromatic Radical," by M L Galashina and N N Mel'nikov, appearing in Zhur Obshchei Khim 23, 1539-42 (1953).

2. The compounds described in this publication are also Parathion types, but appear to be less active and less toxic than Parathion itself. The molecules in the compounds under discussion are too large to be readily volatile and hence they are impractical for use as a nerve gas.

3. Along these same lines, A Ya Yakubovich and S V Motsarev have recently published a paper on the Synthesis of Hetero-organic Compounds of the Aromatic Series by the Reaction of Arylsilanes with Aluminum Chloride and Halides of Various Elements, I, Organophosphorus Compounds, in Zhur Obshchei Khim 23, 1547-52 (1953). This article is merely an elaboration and more complete version of an earlier and shorter form which appeared in Doklady Akad Nauk SSSR 88, 87 (1953). There does not seem to be anything particularly significant about either version of the article.

25X1X 4. Of possible interest, however, is the addition of two more Soviet researchers in the general field. [redacted] V K Kuskov and T Kh Gradis of the M V Lomonosov State University, Moscow, who have recently published an article on the Reaction of Diethyl Phosphite with Sodium Alcoholates, in Doklady Akad Nauk SSSR 92,

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25X1X 323-4 (1953). These two Soviet scientists are entirely new [redacted] 25X1X this is the first time [redacted] ever seen them mentioned; or that [redacted] ever read any publication of theirs. The work described in their article is an amplification or a modification of the method of making organic phosphite [redacted] which Arbuzov has used in the USSR. In other words, [redacted] the work of Kuskov and Gradis is a new modification of that method. Organic phosphites are used as intermediates in the making of other phosphorous compounds. Here again, these organic phosphites possess large molecules and are useful in making insecticides, but would not be useful in making such compounds as nerve gas because they are not readily volatile. 25X1X 25X1X 25X1X 25X1 25X1

5. Because the three Soviet articles [redacted] mentioned above supplement the earlier publications along these lines, [redacted] translated and digested the aforesaid publications in the order in which they are hereinabove listed, as follows: 25X1X 25X1X

A series of aryl-substituted thiophosphates were prepd. All were less active insecticides than Parathion. The compounds were prepd by the coupling of $(RO)_2PSCl$ with ArONa. Generally increase of the size of the OR radical decreased the insecticidal action. Replacement of NO_2 by CNS group greatly reduced insecticidal activity. Introduction of halogens slightly raised insecticidal activity. The preps were made in PhCl suspension with a few drops of pyridine as catalyst at 110-30°. The following were prepd: 24% $(EtO)_2PS(OC_6H_4OMe\text{-}o)$, b_8 170-4°, d_{20} 1.1672, n_D^{20} 1.5990; m-analog, 56%, $b_{0.02}$ 97°, d_{20} 1.1483, n_D^{20} 1.5050; $(EtO)_2PS$-$(OC_6H_4OEt\text{-}m)$, 21%, b_8 170-80°, d_{20} 1.1288, n_D^{20} 1.5045; its PrO analog, 26%, b_8 170-80°, d_{20} 1.1020, n_D^{20} 1.5038; its BuO analog, 17%, $b_{0.35}$ 140-50°, d_{20} 1.1001, n_D^{20} 1.5028; its $PhCH_2O$ analog, 25%, $b_{0.05}$ 140-5°, d_{20} 1.1645, n_D^{20} 1.5620; $(PrO)_2PS$-$(OC_6H_4OMe\text{-}o)$, 24%, $b_{0.05}$ 117°, d_{20} 1.1288, n_D^{20} 1.5120; its m-analog, 18%, b_3 130-50°, d_{20} 1.1106, n_D^{20} 1.4942; its m-EtO analog, 18%, $b_{0.05}$ 110-8°, d_{20} 1.0949, n_D^{20} 1.4920; its m-PrO analog, 25%, $b_{0.35}$ 120-46°, d_{20} 1.0754, n_D^{20} 1.5040; $(EtO)_2PS$-$(OC_6H_4OMe\text{-}p)$, 46%, $b_{0.1}$ 117-22°, d_{20} 1.1910, n_D^{20} 1.5180; its OEt analog, 23%, $b_{0.1}$ 135-40°, d_{20} 1.1400, n_D^{20} 1.5140; its PrO analog, 22%, $b_{0.3}$ 136°, d_{20} 1.1086, n_D^{20} 1.5080; its BuO analog, 46%, $b_{0.2}$ 153°, d_{20} 1.0905, n_D^{20} 1.5082; $(EtO)_2PS$-$(OC_6H_3(OEt)Br\text{-}4,2)$, 20%, $b_{0.02}$ 142-50°, d_{20} 1.3596, n_D^{20} 1.5410; its 2-Cl analog, 11%, $b_{0.15}$ 110-26°, d_{20} 1.2391, n_D^{20} 1.5285; $(EtO)_2PS(OC_6H_4CNS\text{-}p)$, 10%, $b_{0.04}$ 130°, d_{20} 1.2121, n_D^{20} 1.5510; $(MeO)_2PS(OC_6H_4OEt\text{-}m)$, 18%, $b_{0.02}$ 100-7°, d_{20} 1.1970, n_D^{20} 1.5280; $(PrO)_2PS(OC_6H_4OMe\text{-}p)$, 48%, $b_{0.07}$ 124°, d_{20} 1.1201, n_D^{20} 1.5100; its EtO analog, 52%, $b_{0.025}$ 112-20°, d^{20} 1.0956, n_D^{20} 1.5070; its PrO analog, 10%,

$b_{0.2}$ 148-50°, d_{20} 1.0221, n_D^{20} 1.4970; its BuO analog, 30%, $b_{0.025}$ 112-20°, d_{20} 1.0082, n_D^{20} 1.4950; $(PrO)_2PS(OC_6H_3(OEt)Br\text{-}4,2)$, 35%, $b_{0.05}$ 136-40°, d_{20} 1.3113, n_D^{20} 1.5290; its 2-Cl analog, 19%, $b_{0.05}$ 121-6°, d_{20} 1.1883, n_D^{20} 1.5285.

$ArSiCl_3$ react with $AlCl_3$ forming apparently $SiCl_4$ and $ArAlCl_2$; if the reaction mixture is treated with PCl_3, the latter substance reacts, yielding $ArPCl_2$ and $AlCl_3$. If PCl_5 is the reagent, the product is $ArPCl_4$ and $AlCl_3$ in the form of a complex. With $POCl_3$ the complex yields $ArPCl_4$ and $AlCl_3POCl_3$; treatment with SO_2 converts $ArPCl_4$ to $ArPOCl_2$, thus affording a convenient method of prepn of various aryl organophosphorus compounds. Heating 100 g $PhSiCl_3$, 69.3 g $AlCl_3$ and 65 g PCl_3 2 hrs at 80°, followed by distn of $SiCl_4$ under reduced pressure (94.4%), and slow addn to the viscous residue of 85.8 g $POCl_3$ gave a granular ppt of $AlCl_3$, $POCl_3$ complex. This was sepd and washed with petr ether, the washings combined with the filtrate gave 83.4% $PhPCl_2$, b_{57} 140-1°, d_{20}^{20} 1.3180. A mixture of 20 g $PhSiCl_3$ and 13.9 g $AlCl_3$ heated 10 hrs to 70-80°, then freed of $SiCl_4$ in vacuo, (87% obtained), was treated slowly with 13 g PCl_3; the liquid mass was kept 1 hr at 80-90°, then was treated with 17.2 g $POCl_3$; the above procedure of isolation gave 76% $PhPCl_2$, b_{56} 140°. Heating 10 g Ph_2SiCl_2, 11.6 g $AlCl_3$, and 11 g PCl_3 3 hrs at 80°, followed by distn of $SiCl_4$ (92.7%), and treatment with 14.3 g $POCl_3$ gave 80.4% $PhPCl_2$, b_{55} 138-9°. $p\text{-}ClC_6H_4SiCl_3$ (10 g), 6 g $AlCl_3$ and 5.7 g PCl_3 heated 2 hrs at 80°, freed of $SiCl_4$ by distn (90.7%), and treated with 7 g $POCl_3$ gave 6.6 g (77.4%) $p\text{-}ClC_6H_4PCl_2$, b 252-3°, d_{20}^{20} 1.4203. Similarly $p\text{-}BrC_6H_4SiCl_3$ gave 72.6% $p\text{-}BrC_6H_4PCl_2$, b 270°, d_{20}^{20} 1.6801; this added to H_2O gave $p\text{-}BrC_6H_4PO_2H_2$, m 142.3° (from dil EtOH). $p\text{-}MeC_6H_4SiCl_3$ similarly gave 85.3% $p\text{-}MeC_6H_4PCl_2$, b 243-4°, m 24.5°. To 30.2 g $AlCl_3$ and 39.4 g PCl_5 was added with stirring 40 g $PhSiCl_3$ and the mixture was kept 2 hrs at 80-5° (2 layers form); after distn of $SiCl_4$ under reduced pressure (89.6% recovered), the cooled residue was treated slowly with 38.2 g $POCl_3$ and kept 1 hr at 70°, after which the mass was dild with 40 ml CCl_4 and treated with SO_2 until heat evolution ceased. The liq portion was sepd and distd yielding, after removal of $SOCl_2$, 4 g $PhSiCl_3$, b 193-9°, and

19.6 g (18.8 g pure; 45.6%) $PhPOCl_2$, b 250-9° (crude), b 256-8° (pure), d^{20}_{20} 1.3700. Heating 30 g $PhSiCl_3$ and 20.7 g $AlCl_3$ 4 hrs at 80°, followed by cooling to 30° and addn of 68.7 g $POCl_3$, heating 1 hr at 80°, removal of low boiling materials in vacuo and distn of the residue, gave 14.2 g $SiCl_4$, 31.2 g $POCl_3$ and intermediate fractions. The semisolid residue was extd with petr ether, and the combined exts on distn gave 5 g $POCl_3$ and 10 g $PhSiCl_3$, leaving a residue which reacted vigorously with H_2O. Thus $POCl_3$ in contrast to PCl_5 does not react with $PhAlCl_2$.

Heating $(EtO)_2POH$ with various alcs in the presence of the corresponding RONa only transesterification takes place, yielding $(RO)_2POH$. Yields of 85% are common with only a small amount of RONa being necessary, although the use of even molar quantities of the catalyst fails to change the course of the reaction. Thus 0.3 mole ROH containing 0.2 g Na was mixed with 13.8 g $(EtO)_2POH$ and heated under a simple fractionating column until the vapor temp was maintained at 90-5°, gave the desired $(RO)_2POH$. Thus were prepd $(PrO)_2POH$, 86%, b_4 70-2°; $(BuO)_2POH$, 84.5%, b_{10} 115°; (iso-BuO)$_2$POH, 87%, b_{13} 111-13°; (iso-AmO)$_2$POH, 88%, b_3 99-100°; $(C_6H_{11}O)_2$-POH, 70%, b_3 152-3°, the latter prepn of the cyclohexyl deriv required bath temp 160-90°; the others gave good results at somewhat lower temps. The results are quite contrary to those claimed by M Janczak or M Janczakowna (Rozniki Chem 6, 110 (1926), and 4, 180 (1924)) who reported formation of Et_2O and (EtO)P(O)(H)ONa. The prepn of $(EtO)_3P$ and (EtO)P(O)(OH)ONa reported by J is also in doubt.

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